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Long Range Spin-spin Coupling in Kojato Complexes of Tin (IV) and Their Infrared Spectra

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The long range spin-spin coupling was observed between the 3-proton and tin in bis(kojato)-dihalogenotin(IV) and -methylhalogenotin. This observation suggests that the long range spin-spin coupling occurs more strongly through the carbon-oxygen double bond than through the carbon-oxygen single bond. The magnitude of $J_{H_3\text{-}Sn}$ decreases with decreasing Sn-O stretching frequency. The stretching frequency of the Sn-O bond in the kojato complexes of tin was found to be close to those in the tropolonato and oxinato complexes of tin(IV), which also have five membered chelate rings. The configuration of bis(kojato)dimethyltin was suggested to be a distorted octahedral trans-configuration on the basis of the coupling constant of methyl protons with tin and the infrared spectrum.

Introduction

The proton magnetic resonance spectra of bis(acetylacetonato)-dihalogenotin(IV) and -methylhalogenotin show the long range spin-spin coupling of the γ and the methyl protons with tin.[1,2] If a kojato ligand coordinates to tin(IV) as a bidentate ligand, the long range spin-spin coupling might be expected between the proton H_3 or H_6 and tin in the kojato complexes of tin (Figure 1), because these protons are separated by four bonds from the tin atom as the γ and the methyl protons in the acetylacetonato complexes of tin. This paper reports the long range spin-spin coupling and infrared spectra of the kojato complexes of tin, together with a configuration of bis(kojato)dimethyltin.

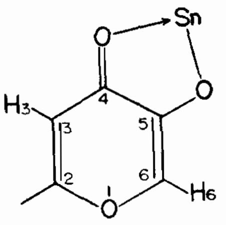

Figure 1. Kojato complex of tin.

Experimental Section

The infrared spectra in nujol and hexachlorobutadiene mulls were measured by a Hitachi EPI-2G (2.5-15 μ) and a Hitachi EPI-L (15-50 μ) grating spectrometers.

The measurements of the proton magnetic resonance spectra were carried out in dimethylsulfoxide (DMSO) solution by a Japan Electron Optics spectrometer model JNM-3H-60 operating at 60 Mc/s at room temperature. The long range spin-spin coupling, however, was observed at 60°C, because DMSO is too viscous to get enough resolution for detecting it at room temperature.

Bis(kojato)dichlorotin. Aqueous solutions of tin tetrachloride (2.6 g, 0.01 mole) and of kojic acid (2.8 g, 0.02 mole) were mixed to give white precipitates, which were recrystallized from methanol.

Bis(kojato)dibromotin. Tin tetrabromide (4.3 g, 0.01 mole) and kojic acid (2.8 g, 0.02 mole) were dissolved in 100 ml methanol and refluxed for 30 minutes. After distilling off the solvent, white precipitates were obtained and purified by recrystallization from methanol.

Bis(kojato)-methylchlorotin and -methylbromotin. Methyltin oxide (1.6 g, 0.1 mole) were dissolved in aqueous hydrochloric acid (0.03 mole) by stirring for a day. Kojic acid (2.8 g, 0.02 mole) was added to this solution to yield white precipitates of bis(kojato)methylchlorotin immediately, which were recrystallized from methanol. Bis(kojato)methylbromotin was prepared by the analogous method.

Bis(kojato)dimethyltin. To an aqueous solution of dimethyltin dichloride (2.2 g, 0.01 mole) and kojic acid (2.8 g, 0.02 mole), a few drops of aqueous ammonia were added. White precipitates appeared gradually and were recrystallized from methanol.

The analytical data and the melting points of these complexes are summarized in Table I.

Results and Discussion

IR Spectra. The relevant infrared frequencies of kojic acid and its complexes of tin are shown in Table II. Free kojic acid shows four bands at 1661-1582 cm^{-1}, one of which should be assigned to the C=O stretching

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(1) Y. Kawasaki and T. Tanaka, *J. Chem. Phys.*, *43*, 3396 (1965).
(2) Y. Kawasaki, *J. Inorg. Nuclear. Chem.*, *29*, 840 (1967).

Table I. Analytical Data and Melting Points of Kojato Complexes of Tin

	M.p. (°C)	% Sn Found (Calcd.)	% C Found (Calcd.)	% H Found (Calcd.)
Cl_2SnKj_2 [a]	>250	25.21 (25.16)	30.53 (30.55)	2.33 (2.14)
Br_2SnKj_2	>250	20.64 (21.17)	25.42 (25.70)	1.97 (1.80)
$(CH_3)ClSnKj_2$	205-208 [b]	26.19 (26.29)	34.58 (34.59)	3.24 (2.91)
$(CH_3)BrSnKj_2$	113-114 [b]	23.81 (23.94)	31.40 (31.49)	2.89 (2.65)
$(CH_3)_2SnKj_2$	194-195.5 [b]	27.22 (27.54)		

[a] Kj = $C_6H_6O_4^-$. [b] Decomposition.

Table II. Relevant IR Frequencies of Kojic Acid and Kojato Complexes of Tin

	ν (C=O) and the others				ν (Sn-O)	ν (Sn-C)	ν (Sn-X) [a]
Kojic Acid	1661 vs	1634 vs	1608 vs	1582 vs			
Cl_2SnKj_2	1621 vs	1565 vs	1553 vs	1515 vs	582 vs		336 vs 331 sh
Br_2SnKj_2	1616 vs	1565 vs	1558 vs	1515 vs	578 vs		268 vs 262 vs
$(CH_3)ClSnKj_2$	1621 vs	1575 vs	1563 vs	1511 vs	572 vs	522 m	304 s
$(CH_3)ClSnKj_2$	1621 vs	1575 vs	1555 vs	1515 vs	572 vs	523 s	265 s
$(CH_3)_2SnKj_2$	1623 vs	1575 vs	1546 vs	1534 vs	552 vs	583 s 504 vw	

[a] X = Cl or Br. vs, very strong; s, strong; m, medium; sh, shoulder; vw, very week.

Table III. PMR Spectra of Kojic Acid and Kojato Complexes of Tin

	τ_{CH_3} [a] (ppm)	$J_{CH_3\text{-}^{119}Sn}$ (cps)	τ_{H_6} (ppm)	τ_{H_3} (ppm)	$J_{H_3\text{-}Sn}$ [b] (cps)
Kojic Acid			1.94	3.62	
Cl_2SnKj_2			1.15	2.84	7.8
Br_2SnKj_2			1.24	2.82	6.0
$(CH_3)ClSnKj_2$	9.28	114.0	1.45	3.05	4.5
$(CH_3)BrSnKj_2$	9.15	111.0	1.41	2.99	4.5
$(CH_3)_2SnKj_2$	9.67	83.3	1.46	3.36	

[a] τ_{values} are taken from an internal tetramethylsilane (10.0 ppm). [b] Measured at 60°C.

vibration. The corresponding bands in the kojato complexes of tin appear at somewhat lower frequencies (1625-1510 cm^{-1}), suggesting the coordination of carbonyl oxygen to the tin atom.

The Sn-O stretching vibrational bands are observed in the region of 585-550 cm^{-1} and can easily be sorted out from the Sn-C stretching vibrational bands because of their characteristic strong and broad bands. The Sn-O stretching frequency decreases in the order; $Cl_2SnKj_2 > Br_2SnKj_2 > (CH_3)ClSnKj_2 \approx (CH_3)BrSnKj_2 > (CH_3)_2SnKj_2$, which is parallel with the order of decreasing electronegativity of the substituents on the tin atom. The Sn-O stretching frequency of the kojato complexes of tin is close to those of the tropolonato (590-550 cm^{-1})[3] and oxinato (540-515 cm^{-1})[4] complexes of tin, but much higher than that of acetylacetonato complexes (460-400 cm^{-1}).[5] The similar Sn-O bond character is, therefore, expected for the complexes of tin with five membered chelate rings.

PMR Spectra. The chemical shifts of the methyl protons attached to the tin atom and the ring protons in the kojato complexes of tin, together with those of kojic acid, in DMSO solution are shown in Table III. The assignment of the proton signals of kojato ring was made according to the Varian NMR Spectra Catalog.[6]

The long range spin-spin coupling of the 3-proton with tin ($J_{H_3\text{-}Sn}$)* was observed in the kojato complexes of dihalogenotin and methylhalogenotin, the values of which are also shown in Table III. However, the coupling of the 6-proton with tin ($J_{H_6\text{-}Sn}$) has not been detected, which might be included in the bottom of the 6-proton signal, and then its magnitude would be less than 3 cps. Neither long range spin-spin coupling ($J_{H_3\text{-}Sn}$ and $J_{H_6\text{-}Sn}$) was found in bis(kojato)dimethyltin.

The coupling constant, $J_{H_3\text{-}Sn}$, decreases with decreasing Sn-O stretching frequency. These results are compared with those obtained in acetylacetonato complexes of tin.[2] The present observations of the coupling only between the 3-proton and tin suggest that the long range spin-spin coupling occurs more strongly through the π-electron system of the carbon-oxygen double bond than through the σ-electron system of the carbon-oxygen single bond in the kojato complexes of tin.** This is consistent with the mechanism proposed for the long range spin-spin coupling in bis(3-methylacetylacetonato)dibromotin,[7,8] (acetylacetonato)trimethylplatinum complexes[7] and many organic unsaturated molecules.[9-12]

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(3) M. Komura, T. Tanaka and R. Okawara, to be published.

(4) M. Komura, Y. Kawasaki and T. Tanaka, unpublished data.

(5) Y. Kawasaki, T. Tanaka and R. Okawara, *Spectrochim. Acta*, *22*, 571 (1966).

(*) $J_{H_3\text{-}^{119}Sn}$ and $J_{H_3\text{-}^{117}Sn}$ could not been resolved.

(**) Since the difference between the hybridization states of the 3- and 6-carbons would be small, the present results may well be interpreted in terms of the difference between the carbon-oxgen bond characters.

(6) High Resolution NMR Spectra Catalog, Vol. 2 (Varian Associates, Palo Alto, California, 1963).

(7) K. Kite, J. A. S. Smith and E. J. Wilkins, *J. Chem. Soc.*, (A), 1744 (1966).

(8) J. A. S. Smith and E. J. Wilkins, *J. Chem. Soc.*, (A), 1749 (1966).

(9) R. A. Hoffman, *Mol. Phys.*, *1*, 326 (1958).

(10) E. B. Whipple, J. H. Goldstein and W. E. Stewart, *J. Am. Chem. Soc.*, *81*, 4761 (1959).

(11) M. Karplus, *J. Chem. Phys.*, 33, 1842 (1960).

(12) S. Sternhell, *Rev. Pure and Appl. Chem.*, *14*, 15 (1964).

The coupling constants of methyl protons with tin ($J_{CH_3\text{-}^{119}Sn}$) in bis(kojato)-dimethyltin and -methylhalogenotin are also shown in Table III. In the methylhalogenotin complexes, the coupling constant is larger than that in the dimethyltin complex. This may be caused by the increase in the s-character of the Sn-C bond by the rehybridization of the tin orbital in the former complexes.[13]

Configuration of Bis(kojato)dimethyltin. The infrared spectrum of bis(kojato)dimethyltin shows two Sn-C stretching vibrational bands at 584 and 504 cm^{-1}, which can be assigned to the asymmetric and symmetric stretching modes, respectively, suggesting that the C-Sn-C moiety does not have a linear configuration. In the proton magnetic resonance spectra of methyltin compounds, the coupling constant of methyl protons with tin ($J_{CH_3\text{-}^{119}Sn}$) is found to be 54.0 cps for tetramethyltin[14] with tetrahedral angle of the C-Sn-C moiety and 99.3 cps for bis(acetylacetonato)dimethyltin[15] with the linear C-Sn-C moiety. The $J_{CH_3\text{-}^{119}Sn}$ value of 83.3 cps in bis(kojato)dimethyltin, therefore, suggests that the angle of the C-Sn-C moiety is between the tetrahedral and dihedral angles. This may rule out a *cis*-configuration with the C-Sn-C moiety of the right angle. The most probable one may be a distorted octahedral *trans*-configuration as shown in Figure 2; two carbonyl oxygen atoms coordinate to the tin atom from the same side and two Sn-C bonds incline to this side. This configuration is analogous to that proposed for bis(dithiocarbamato)dimethyltin ($J_{CH_3\text{-}^{119}Sn} = 84.0$ cps) on the basis of the solvent shift in the proton magnetic resonance spectrum.[16]

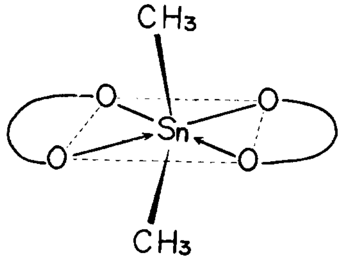

Figure 2. Configuration of bis(kojato)dimethyltin.

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[13] H. A. Bent, *Chem. Revs.*, *61*, 275 (1961).

[14] J. R. Holmes and H. D. Kaesz, *J. Am. Chem. Soc.*, *83*, 3903 (1961).

[15] M. M. McGrady and R. S. Tobias, *J. Am. Chem. Soc.*, *87*, 1909 (1965).

[16] M. Honda, Y. Kawasaki and T. Tanaka, Tetrahedron Letters, 3313 (1967).